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Changes in the source of nutrients associated with oceanographic dynamics offshore southern Chile (41°S) over the last 25,000 years

Thomas J. Verleye [a,b,*], Philippe Martinez [c], Rebecca S. Robinson [d], Stephen Louwye [a]

[a] Research Unit Palaeontology, Department of Geology and Soil Science, Ghent University, Krijgslaan 281 S8/WE13, 9000 Ghent, Belgium
[b] Flanders Marine Institute (VLIZ), Wandelaarkaai 7, 8200 Oostende, Belgium
[c] Université Bordeaux 1, UMR 5805 EPOC, avenue des facultés, 33405 Talence cedex, France
[d] Graduate School of Oceanography, University of Rhode Island, Narragansett, RI 02882, USA

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ABSTRACT

In order to obtain a better knowledge of past oceanographic variability offshore southern Chile, this study reappraises the changes in the sources of nutrients over the last 25 ka based on a detailed comparison of previously published nitrogen isotope and microfossil records (dinoflagellate cysts, coccoliths and diatoms) from ODP Site 1233 (41°S). Our findings support the main conclusions of Martinez et al. (2006) in the sense that both the Subantarctic Surface Water and the Gunther Undercurrent are potential sources for the recorded late Quaternary sedimentary $\delta^{15}N$ signatures at Site 1233, with variable contributions of both sources during different time periods. This study indicates that Subantarctic Surface Water forms the main source for nutrients during the last glacial maximum (25–18.6 cal ka BP), the first part of the deglaciation (18.6–15.7 cal ka BP) and the Holocene (9.8 cal ka BP until present). An increased contribution of Equatorial Subsurface Water as a source of nutrients to the photic zone offshore southern Chile is observed between 14.4 and 9.8 cal ka BP, which is indicative for upwelling conditions at least after 13.2 cal ka BP as indicated by the microfossil data.

Introduction

Nitrogen (N), and mainly nitrate, is one of the main elements regulating marine biological productivity variations in nutrient limited environments such as the low- and mid-latitude oceans (e.g., Hebbeln et al., 2000, 2002; Mohtadi and Hebbeln, 2004; Sarmiento et al., 2004; Pisias et al., 2006; Romero et al., 2006; Mohtadi et al., 2008; Verleye and Louwye, 2010a; Saavedra-Pellitero et al., 2011). At present, nitrate is not completely consumed in the Southern Ocean where the uptake is limited by other factors such as light and the absence of micronutrients (mainly iron) (e.g., Mitchell et al., 1991). This results in a CO_2 efflux from the ocean to the atmosphere. Recent studies indicate that the nutrient load of the Antarctic Circumpolar Current (ACC) during the last glacial maximum was lower than today as a result of a 30% increase in nutrient consumption by phytoplankton in the Southern Ocean (Robinson et al., 2005), which should have limited the release of CO_2 (e.g., Sigman and Boyle, 2000). Nitrate is ultimately removed from the marine ecosystem by microbial denitrification which occurs in oxygen-poor sediments and in suboxic (<5 μM O_2) water columns of the open-ocean oxygen minimum zones, housed in the eastern (sub)tropical North and South Pacific and the Arabian Sea. Besides the regulation of biological production, nitrate removal in oxygen minimum zones also directly impacts global climate by the reduction of nitrate into the greenhouse gas nitrous oxide (N_2O), which has a tremendous global warming potential.

During the phytoplankton assimilation and the microbial denitrification, the lighter (^{14}N) isotope preferentially undergoes reaction. As the initial nitrate supply is progressively consumed, the $^{15}N/^{14}N$ of the remaining nitrate increases which leads to a related increase in the N isotopic ratio of the organic matter itself. In the Subantarctic Zone, for instance, the nutrients are supplied through northward lateral advection from the Antarctic Zone and are progressively consumed (Altabet and François, 1994; Sigman et al., 1999) causing a steep north–south nitrate gradient from ~20 μM at the Subantarctic Front to ~4 μM at the Subtropical Front (Garcia et al., 2010a). This equatorward decrease in nitrate availability is accompanied by an increase in the N isotope ratio $\delta^{15}N$ ($\delta^{15}N = [(^{15}N/^{14}N_{sample})/(^{15}N/^{14}N_{reference}) - 1] \times 1000$, with the atmospheric N_2 as the universal reference) of the nitrate pool and of the organic matter produced by phytoplankton. When the surface nutrients are completely consumed, sedimentary $\delta^{15}N$ is a reflection of the isotopic composition of the nitrate delivered to the surface waters.

In this study, we first compare the sedimentary nitrogen isotope record (25–0 cal ka BP) (Martinez et al., 2006) from ODP Site 1233 (41°S; offshore southern Chile) with high-resolution dinoflagellate cyst assemblage data from Verleye and Louwye (2010a), with additional microfossil records from Mix et al. (2003) and Saavedra-Pellitero et al. (2011) in

* Corresponding author at: Research Unit Palaeontology, Department of Geology and Soil Science, Ghent University, Krijgslaan 281 S8/WE13, 9000 Ghent, Belgium. Fax: +32 59 34 21 31.
E-mail address: thomas.verleye@vliz.be (T.J. Verleye).

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order to give a better constrained interpretation of the nutrient source changes off southern Chile since the last glaciation. A comparison with sedimentary nitrogen isotope records from cores located north and south of our study area (GeoB7139-2 (30°S), De Pol-Holz et al., 2006; E11-2 (54°S), Robinson et al., 2005) gives additional insights into the two main water mass end-members feeding the Southern Chile margin.

ODP Site 1233 is located at the southern margin of the South Pacific eastern boundary current, which is one of the world's most productive marine environments (Berger et al., 1987) (Fig. 1a), and is strongly influenced by both high- and low-latitude biogeochemical processes. The eastern tropical South Pacific houses a large region of water-column denitrification that accounts for approximately 15% of the total N removal from the ocean and distributes ^{15}N-enriched water toward the south and west in the Pacific (Martinez et al., 2006; Robinson et al., 2007; Kienast et al., 2008; Robinson et al., 2009; Martinez and Robinson, 2010) while less ^{15}N-enriched surface waters are advected from the Southern Ocean (Fig. 1c). Martinez et al. (2006) suggested that the sedimentary $\delta^{15}N$ at ODP Site 1233 reflects the isotopic composition of the nitrate delivered to the region. Therefore, the recorded $\delta^{15}N$ values and nitrate concentrations at Site 1233 depend on the oceanographic dynamics in the source areas and the regional/local oceanographic changes such as upwelling, stratification and the position of the Subtropical Front. This dynamical process regulates the contribution of both the Subantarctic Surface Water (SASW) and the Gunther Undercurrent (GUC) in influencing at once the $\delta^{15}N$ signature and nitrate availability at Site 1233.

The microfossil data makes a valuable contribution in validating that an increasing influence of SASW lowers nitrate concentrations and might also lower the $\delta^{15}N$ signature, while a greater GUC contribution likely has the opposite effect. A comparison with late Quaternary nitrogen isotope records derived from cores north and south of the study area is therefore crucial. In this respect, the record of core E11-2 (54°S) can be interpreted as a Subantarctic end-member and can be indicative for the influence of SASW at Site 1233.

Martinez et al. (2006) suggested that high $\delta^{15}N$ values between 19 and 10 cal ka BP reflected a stronger lateral advection of heavy nitrates from the more northerly denitrification zones offshore of Peru and northern Chile, while lower isotopic compositions during the Holocene and the last glacial maximum were assumed to be largely controlled by Southern Ocean dynamics. A better understanding of past local oceanographic variability, as obtained by microfossil analyses, can provide more detailed information about the source area of the recorded sedimentary organic matter $\delta^{15}N$ at Site 1233.

Regional setting

Surface circulation in the SE Pacific offshore Chile is dominated by the equatorward flowing Peru–Chile Current, originating between 40°S and 45°S as a northern branch of the ACC (Boltovskoy, 1976; Strub et al., 1998) (Fig. 1a). North of 35°S, the Peru–Chile Counter Current divides the northward-flowing Peru–Chile Current into a coastal and oceanic branch, which turns off to the west close to the equator to form the South Equatorial Current (Fig. 1a). The ACC, in turn, is a high-nutrient low-chlorophyll area, in which biological productivity is limited by the absence of micronutrients, such as iron (De Baar et al., 1995; Boyd et al., 2000, 2001; Hutchins et al., 2001). The high river discharges associated with hyper-humid conditions of onshore southern Chile result in an increase of iron availability in the coastal surface waters, which in turn increases primary productivity (e.g., Iriarte et al., 2007).

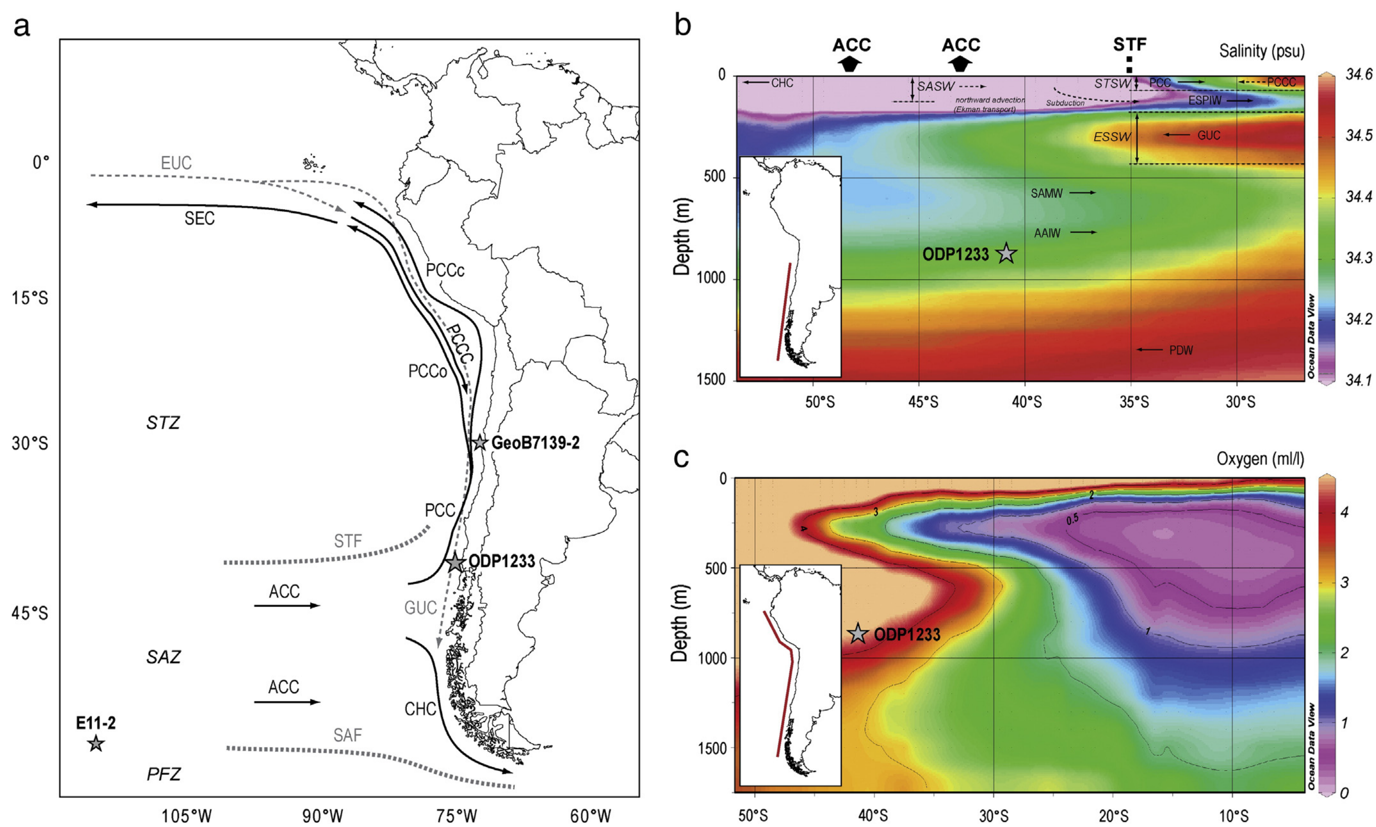

Figure 1. Oceanography of the SE Pacific. (a) Surface currents in the SE Pacific and the location of ODP Site 1233 and other cores (GeoB7139-2, E11-2); (b) vertical profile of the main currents in the upper 1500 m of the SE Pacific between 32°S and 53°S and their salinity characteristics; (c) oxygen concentrations in the upper 1500 m in a vertical profile along a transect in the SE Pacific between 14°S and 51°S. Abbreviations: AAIW, Antarctic Intermediate Water; ACC, Antarctic Circumpolar Current; CHC, Cape Horn Current; ESSW, Equatorial Subsurface Water; EUC, Equatorial Undercurrent; GUC, Gunther Undercurrent; PCC, Peru–Chile Current; PCCc, coastal branch of Peru–Chile Current; PCCo, oceanic branch of the Peru–Chile Current; PCCC, Peru–Chile Counter Current; PDW, Pacific Deep Water; PFZ, Polar Frontal Zone; SAF, Subantarctic Front; SAMW, Subantarctic Mode Water; SASW, Subantarctic Surface Water; SAZ, Subantarctic Zone; SEC, South Equatorial Current; STF, Subtropical Front; STSW, Subtropical Surface Water; STZ, Subtropical Zone.

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The availability of both macro- and micronutrients elevates productivity offshore southern Chile above that of the upwelling-dominated parts offshore central/north Chile (Hebbeln et al., 2000).

The ACC is bounded to the north by the Subtropical Front, separating the northern ACC waters (Subantarctic Surface Water; SASW) from the warm, nutrient-depleted Subtropical Surface Water (STSW) (Figs. 1a and b). Just south of the Subtropical Front, subduction of the less saline and colder SASW (~34 psu) underneath the more saline STSW (34.5 psu) results in the formation of the Eastern South Pacific Intermediate Water, which, when farther north, is characterized as a shallow, thin-salinity minimum layer between the STSW and the Equatorial Subsurface Water (ESSW) (Tsuchiya and Talley, 1998; Schneider et al., 2003) (Fig. 1b).

The Peru–Chile Current and Eastern South Pacific Intermediate Water are underlain by the oxygen-poor and nutrient-rich GUC (100–300 m water depth), which originates from the eastward-flowing Equatorial Undercurrent (also called the Cromwell Current) (Cromwell, 1953) (Figs. 1a and b). The GUC transports ESSW from the tropics toward 48°S (Fonseca, 1989) and forms the source for the upwelled waters north of 40°S (Morales et al., 1996). The GUC currently carries oxygen-poor water bearing nitrate with a high δ^{15}N signature poleward (Fig. 1c). The GUC, in turn, is underlain by the relatively low-saline and oxygen-rich Subantarctic Mode Water and Antarctic Intermediate Water, which are vertically located between 300 and 1200 m water depth (Tsuchiya and Talley, 1996; Strub et al., 1998; Tsuchiya and Talley, 1998). Into the deep ocean, the Pacific Deep Water is a slow, southward-flowing current between ~1200 and ~3400 m water depth, which is in the deepest parts underlain by the oxygen-rich northward flowing Antarctic Bottom Water (Ingle et al., 1980; Shaffer et al., 1995; Garcia et al., 2010b) (Fig. 1b).

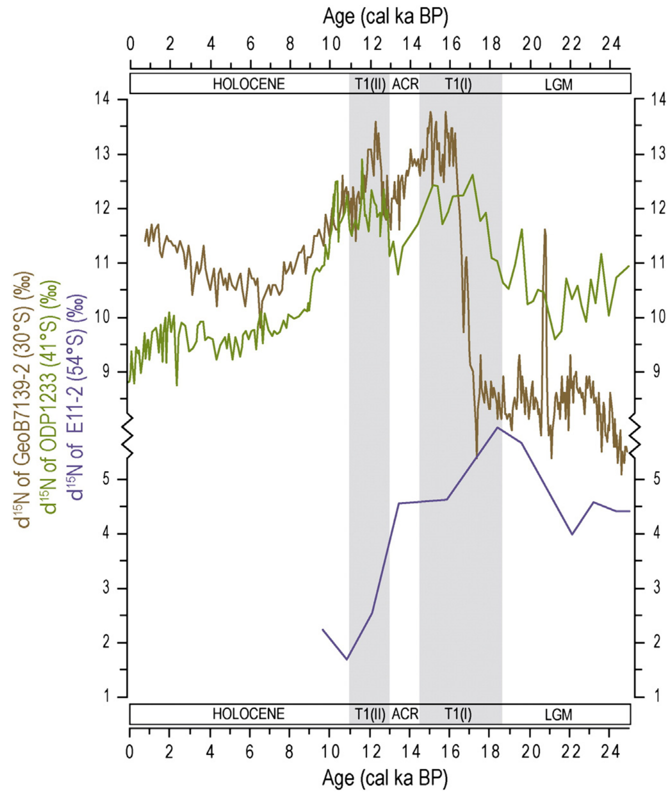

Figure 2. δ^{15}N records of cores GeoB7139-2, located in the SE Pacific (30°S) (De Pol-Holz et al., 2006); ODP 1233, located in the SE Pacific (41°S) (Martinez et al., 2006); E11-2, located in the southern part of the Subantarctic Zone (Robinson et al., 2005).

Material and methods

ODP Site 1233

The ODP Site 1233 is located 40 km offshore southern Chile (41°0.01′ S, 74°26.99′W) in a small fore-arc basin on the upper continental slope at 838 m water depth (Mix et al., 2003). Exceptionally high sedimentation rates between 1 and 3 m ka^{-1} are recorded during the late Quaternary and favor the good preservation of organic-, siliceous- and $CaCO_3$-walled microfossils in the marine sediments. The lithology of the studied interval of ODP 1233 is dominated by homogenous olive-brown clayey silts, with a minor amount of well-preserved biogenic components (Mix et al., 2003). The age model has been previously published by Lamy et al. (2004), Kaiser et al. (2005) and Lamy et al. (2007), and is based on 27 ^{14}C Accelerator Mass Spectrometer (AMS) control points on mixed planktonic forminifera samples in the upper 39.5 m (25 cal ka BP), and is converted to calendar years taking into account a reservoir age of 400 years. This age model was also applied to the δ^{15}N record of Martinez et al. (2006), which was initially based on 17 ^{14}C AMS control points and did not include the update of Lamy et al. (2007).

Microfossils and isotopic analyses

We refer to Mix et al. (2003) (diatoms), Verleye and Louwye (2010a) (dinoflagellate cysts) and Saavedra-Pellitero et al. (2011) (coccolithophores) for the palynological preparation procedures of the phytoplankton groups discussed herein. The potential occurrence of syn- and post-depositional processes redistributing sediments on the seafloor may alter mass accumulation rates of sedimentary components (François et al., 2004), and made us decide to study microfossils in concentrations g^{-1} without correcting for sediment accumulation rates. Specifications about the isotopic analyses of δ^{15}N are described in detail by Robinson et al. (2005), De Pol-Holz et al. (2006) and Martinez et al. (2006) for cores E11-2, GeoB7139-2 and ODP 1233, respectively (Fig. 2).

Chronology of cores GeoB7139-2 and E11-2

Similar as for core ODP 1233, ^{14}C AMS dates of core GeoB7139-2 were measured on tests of mixed planktonic foraminifera and corrected for a mean ocean reservoir age of 400 years (Mohtadi and Hebbeln, 2004). The age model for core El1-2 was derived by Ninnemann and Charles (1997), through correlation of the δ^{18}O stratigraphy (*N. pachyderma*) to that of the well-dated, high-resolution core RC11-83.

Results and discussion

Nitrate source switching offshore of southern Chile

Sedimentary δ^{15}N signatures can result from a variety of processes such as the variable supply of land-derived organic material, the degree of nitrate consumption (phytoplankton, microbial) changes in the source of nitrate and/or its isotopic composition, and the preservation of the isotopic signature. Martinez et al. (2006) excluded a significant influence of terrestrial organic matter at Site 1233 based on low C/N ratios (mean = 6.85), close to the Redfield ratio (carbon/nitrogen/phosphorus) of marine particles, and heavy δ^{15}N values (>9‰). Furthermore, the complete or almost complete consumption of nitrate along the southern Chile margin suggests that the sedimentary δ^{15}N offshore of southern Chile (41°S) essentially reflects the isotopic composition of the nitrate delivered to the region (Martinez et al., 2006) (Fig. 2). Both the high sedimentation rate and the good preservation of organic matter on margins imply that sedimentary δ^{15}N accurately records the δ^{15}N of sinking organic matter (Altabet et al., 1999).

According to Martinez et al. (2006), an amalgam of high- and low-latitude processes influences the late Quaternary ODP 1233 δ^{15}N record (Fig. 2). Martinez et al. (2006) proposed that advected nitrates originating from the denitrification zones in offshore Peru and central/northern Chile dominate the δ^{15}N record for the period between 19 and 10 cal ka BP, except during the Antarctic Cold Reversal (ACR) period. However, the δ^{15}N increase in SE Pacific records located offshore of central Chile (De Pol-Holz et al., 2006 [30°S]; Robinson et al., 2007 [36°S]; Mohtadi et al., 2008 [36°S]) lags behind the increase at Site 1233 by ~1.7 ka, and is suggestive of an additional influence between 19 and 17 cal ka BP. Combining the δ^{15}N and environmentally sensitive phytoplankton records (mainly dinoflagellate cysts) can increase our understanding of past oceanographic variability in offshore southern Chile, and may therefore further elucidate the source regions of the advected sedimentary δ^{15}N signatures at Site 1233.

The last glaciation

The last glaciation is characterized by high relative abundances (70–85%) of *Brigantedinium* spp. (Fig. 3c). This dinoflagellate cyst species presently shows a gradual increase in relative abundances in a southward direction across the Subantarctic Zone (Esper and Zonneveld, 2002). This points to a more equatorward position of the ACC during the last glacial maximum. The sedimentary δ^{15}N signature is consistent with this interpretation and points to a cross-frontal northward advection of SASW toward Site 1233, meaning that productivity was fuelled primarily by nutrients advected from the Southern Ocean (Fig. 3a). The poleward undercurrents, such as the GUC, are suggested to be weaker during the last glaciation (Kienast et al., 2002) and possibly limited a subsurface southward transport of lower δ^{15}N waters as far as 41°S. Furthermore, the onshore blowing westerly winds prevented upwelling at Site 1233 during the last glaciation, which would hinder the upward transport of GUC water into the photic zone (Verleye and Louwye, 2010a; Verleye et al., 2011).

The initial δ^{15}N rise at Site 1233 occurs at 21.3 cal ka BP and seems to correspond with the increasing ^{15}N/^{14}N-ratio at core site E11-2 recorded between 22.1 and 19.6 cal ka BP (Fig. 2). This increase corresponds with the first decrease in relative abundances of *Brigantedinium* spp. at 21.4 cal ka BP, as recorded offshore of Chile at 41°S (Fig. 3c). A decrease in relative abundances of this species has been interpreted as a poleward shift of the ACC and its related circumpolar frontal systems (Verleye and Louwye, 2010a), consistent with the inference based on the N isotopes that the nutrients overlying the site are still primarily advected from the Southern Ocean.

Deglaciation (phase 1) and the ACR

An accelerated increase of δ^{15}N values at Site 1233 occurred just after 18.7 cal ka BP, corresponding well with the accelerated decrease in *Brigantedinium* spp. at 18.6 cal ka BP (Figs. 3a and c). The decrease in *Brigantedinium* spp. is consistent with the inferred poleward shift of the ACC (e.g., Lamy et al., 2004; Kaiser et al., 2005; Verleye and Louwye, 2010a). Such a shift implies that Site 1233 will be oceanographically relocated toward the northernmost zone of the Subantarctic Zone. The increase in δ^{15}N at Site 1233 may be due to this relocation. The δ^{15}N increase in more equatorward sites along the South American margin (De Pol-Holz et al., 2006 [30°S]; Robinson et al., 2007 [36°S]; Mohtadi et al., 2008 [36°S]), started much later than at Site 1233: ~17 cal ka BP, or ~1.7 ka later compared to the accelerated increase at Site 1233 (Fig. 2), implying that the increase was not transmitted by the GUC. Instead, the increase in δ^{15}N is likely related to Site 1233's position along the nitrate gradient in the Subantarctic. Despite the overall decrease in consumption in the E11-2 record, the Chile margin was being bathed in waters bearing a high δ^{15}N signal due to enhanced drawdown in the overlying waters related to the shift in the site's position relative to the overlying nitrate field (Robinson et al., 2005). The surface waters were still primarily sourced from the Southern Ocean at this time.

The δ^{15}N increase at Site 1233 lasts until 17.2 cal ka BP. We assume that the δ^{15}N increase until 17.2 cal ka BP is primarily controlled by Southern Ocean dynamics, which agrees with the high abundances of *Brigantedinium* spp. (Fig. 3c), and puts the Subtropical Front north of 41°S. The fairly constant and high numbers of heterotrophs (95%) point to a direct and undisturbed influence of SASW at Site 1233 until at least 15.7 cal ka BP (Fig. 3b). The sharp δ^{15}N increase of 6‰ as observed between 17 and 16 cal ka BP in the northern cores (30°S; 36°S), ascribed to an intensification and southward propagation of the oxygen minimum zone offshore central Chile (De Pol-Holz et al., 2006, 2007; Mohtadi et al., 2008), is not observed at Site 1233. This indicates that if isotopically enriched nitrate was carried southward by the GUC, it was not upwelled, assimilated, and converted to organic N by phytoplankton in significant amounts (Figs. 2 and 3a). This is supported by the low relative abundances of upwelling-associated dinoflagellate cysts, i.e. *Echinidinium aculeatum* (Fig. 3d).

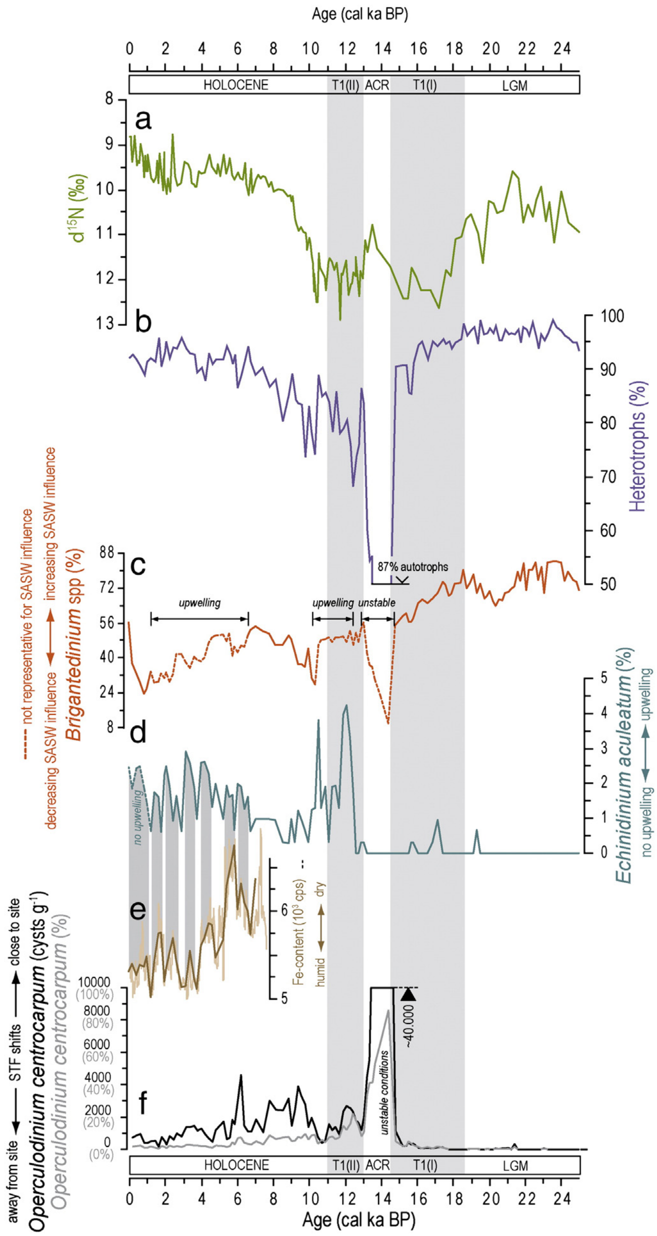

Figure 3. Paleoceanographic records from ODP Site 1233 in the SE Pacific. (a) δ^{15}N record (Martinez et al., 2006); (b) relative abundances of heterotrophic dinoflagellate cysts (Verleye and Louwye, 2010a); (c) relative abundances of *Brigantedinium* spp. (Verleye and Louwye, 2010a); (d) relative abundances of *Echinidinium aculeatum* (Verleye and Louwye, 2010a); (e) high resolution iron contents and iron contents at the respective depths of dinoflagellate cyst analyses (cps) of GeoB3313-1 (= Site 1233) (Lamy et al., 2001); (f) absolute and relative abundances of *Operculodinium centrocarpum* (Verleye and Louwye, 2010a).

During the ACR period, the latitudinal shifts of the Subtropical Front are likely restricted to the area around 41°S (Verleye and Louwye,

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2010a). This is based on the very high absolute and relative abundances of *Operculodinium centrocarpum*, an autotrophic dinoflagellate cyst species often observed in the vicinity of the Subtropical Front (in the southern part of the Subtropical Zone) (Marret et al., 2001; Esper and Zonneveld, 2002) (Fig. 3f). This species may adapt better to changing conditions than other dinoflagellate cysts and is able to cope with extreme seasonality (e.g., Dale, 1983). The ACR period has therefore been interpreted as being unstable likely associated with the vicinity of the Subtropical Front (Verleye and Louwye, 2010a), in which other nanoplankton such as diatoms and coccolithophores seem unable to thrive in large quantities as supported by their low concentrations (Fig. 4). This allows *O. centrocarpum* to take up the remaining nutrients and to bloom (Fig. 3f). A fast southward migration of the westerlies during the first phase of the deglaciation toward 41°S was also suggested by McCulloch et al. (2000), who assumed that they reached a position similar as today around 14.3 cal ka BP.

The δ^{15}N record shows a prominent decline during the ACR period, similar to the observed changes in the north (GeoB7139-2; de Pol-Holz et al., 2006) (Fig. 2). The lower δ^{15}N values at 41°S are therefore more likely transported from the north and supplied into the surface by deep mixing ascribed to the westerlies. The westerlies were probably more intensely associated with a steep latitudinal SST gradient due to a more intense Hadley Cell activity (Thompson et al., 1998) and an extension of the Antarctic sea ice (Bianchi and Gersonde, 2004; Naish et al., 2009). An intensification of the westerly wind belt is also supported by Bertrand et al. (2008), who observed a particular wet phase at Lago Puyehue (40°S) between 15 and 13 cal ka BP. However, it should be noted that there is still uncertainty about the oceanographic and the atmospheric responses at 41°S with respect to the ACR period.

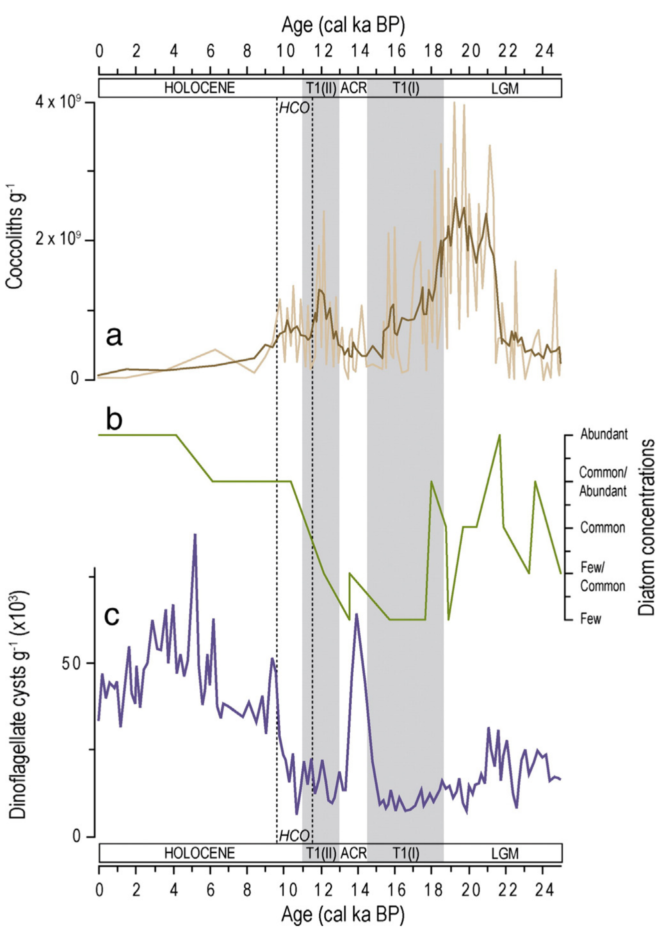

Figure 4. ODP 1233 microfossil records. (a) Coccolithophores g^{-1} (Saavedra-Pellitero et al., 2011); (b) low-resolution diatom record (Mix et al., 2003); (c) dinoflagellate cysts g^{-1} (Verleye and Louwye, 2010a).

Deglaciation (phase 2) and the Holocene

The second phase of the deglaciation and the Holocene climatic optimum (13–9.8 cal ka BP) is characterized by a southward expansion or an intensification of suboxia and denitrification in the SE Pacific (De Pol-Holz et al., 2006; Robinson et al., 2007; Mohtadi et al., 2008) (Fig. 2), a signal that is laterally advected to the south at subsurface depth and recorded up to 41°S (Fig. 2). This time interval is characterized by an increase (up to 4%) of the dinoflagellate cyst *E. aculeatum* (Fig. 2). A core-top study in the SE Pacific demonstrated that this species is related to highly productive regions and/or upwelling regions, while relative abundances from 3% to 9% were exclusively observed in active upwelling cells (Verleye and Louwye, 2010b). The occurrence of upwelling between 13 and 9.8 cal ka BP is also supported by an increase in the abundances of the coccolithophore *Gephyrocapsa oceanica* as demonstrated by Saavedra-Pellitero et al. (2011). A farther southward shift of the ACC and associated westerly wind belt thus allowed upwelling at 41°S during the austral summer and enabled the assimilation of GUC ^{15}N-enriched nitrate (Fig. 2).

A fast drop in δ^{15}N at 41°S compared to the record at 30°S occurred between 9.8 and 7 cal ka BP and might be caused by an equatorward shift of the ACC, according to the dinocyst record (Figs. 2, 3c, d and f). This increases the advection of isotopically lower surface waters originating from the Subantarctic Zone where nutrient utilization was low compared to the last glacial maximum (Robinson et al., 2005). Higher relative abundances of *O. centrocarpum* also support a northward shift of the Subtropical Front toward 41°S (Fig. 3f). Decreasing relative abundances of *E. aculeatum* suggest that upwelling was prevented during this time period and obstructed the upward transport of the isotopically enriched poleward-flowing ESSW (GUC) (Fig. 2). Upwelling may have been hindered by an intensification of the onshore blowing westerlies ascribed to a steepening of the meridional SST gradients. The latter results from an increase in sea-ice extension from ~9 cal ka BP onwards (Bianchi et al., 2004), contemporaneous with the dominance of La Niña-like conditions (until 7 cal ka BP) (Moy et al., 2002), which strengthen the SE Pacific anticyclone.

The δ^{15}N record differs considerably between ODP 1233 and GeoB7139-2 after 7 cal ka BP (Fig. 2). The diverging trends between both records toward the late Holocene suggest a dominant influence from the Southern Ocean on Site 1233. Overall, the lower N isotope ratio during the Holocene, when compared to the last glacial maximum, is similar to the record at E11-2 (Fig. 2). The recorded isotope values in sedimentary organic matter during the mid- to early Holocene seem, however, also to be partially controlled by the subtropical SE Pacific, superimposed on the Southern Ocean influences. During the last 7 ka, *E. aculeatum* fluctuates between 0.5% and 2.5%, with highest relative abundances during periods of lower rainfall, as indicated by the GeoB3313-1 (= Site 1233) iron record of Lamy et al. (2001) (Figs. 3d and e). Those periods are characterized by a weakening or a more southward position of the northern margin of the westerlies, and may thus enable seasonal upwelling at 41°S as indicated by *E. aculeatum*.

A strong relative increase of *Brigantedinium* spp. from ~30% to ~60% (Fig. 3c) and a contemporaneous decrease of *Echinidinium* spp. from ~50% to ~24% (Verleye and Louwye, 2010a) during the last 1 ka point to an increasing influence of the SASW and an absence of upwelling during this time period. The decrease in δ^{15}N during the last 2 ka is consistent with an accelerated northward shift of the ACC and is in agreement with the findings of Mohtadi et al. (2007) (Fig. 3a).

Conclusions

The knowledge of past oceanographic changes as derived from microfossils has proven to contribute significantly to the detailed reinterpretation of the ODP Site 1233 sedimentary δ^{15}N record, and enabled a more precise timing of the periods characterized by different oceanographic conditions. It has been demonstrated that both the SASW and the GUC are a potential source for the recorded sedimentary $\delta^{15}N$ signatures at Site 1233 during the last 25 ka, with variable contributions of both sources during different time periods. Changes in the source of nitrates are related to regional/local oceanographic changes which in turn are controlled by latitudinal shifts of the ACC and the southern westerly wind belt. The combination of geochemical and microfossil data demonstrated that the SASW forms the dominant source during the last glacial maximum, the first phase of the deglaciation until at least 15.7 cal ka BP, and the Holocene (9.8 cal ka BP to present). Periodical seasonal upwelling during the Holocene dry periods, however, resulted in an increase in the contribution of ESSW as demonstrated by this study. The multiproxy approach demonstrated that the latter was the main nutrient source during the upwelling-dominated periods, i.e., the last phase of the deglaciation and the Holocene climatic optimum (13–9.8 cal ka BP). The isotopically heavy nitrates from the ESSW could possibly be transported upwards during the ACR period by deep mixing, ascribed to an intensification of the westerlies.

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References

Altabet, M.A., François, R., 1994. Sedimentary N isotopic ratio as a recorder for surface nitrate utilisation. Global Biogeochemical Cycles 8, 103–116.

Altabet, M.A., Pilskaln, C., Thunell, R., Pride, C., Sigman, D., Chavez, F., François, R., 1999. The N isotope biogeochemistry of sinking particles from the margin of the Eastern North Pacific. Deep-Sea Research I 46, 655–679.

Berger, W.H., Fischer, K., Lai, C., Wu, G., 1987. Ocean productivity and organic carbon flux. Part I. Overview and maps of primary production and export production. SIO References 87–30.

Bertrand, S., Charlet, F., Charlier, B., Renson, V., Fagel, N., 2008. Climate variability of southern Chile since the last glacial maximum: a continuous sedimentological record from Lago Puyehue (40°S). Journal of Paleolimnology 39, 179–195.

Bianchi, C., Gersonde, R., 2004. Climate evolution at the last deglaciation: the role of the Southern Ocean. Earth and Planetary Science Letters 228, 407–424.

Boltovskoy, E., 1976. Distribution of recent foraminifera of the South American region. In: Hedley, R.H., Adams, C.G. (Eds.), Foraminifera. Academic Press, London, pp. 171–237.

Boyd, P.W., Watson, A.J., Law, C.S., Abraham, E.R., Trull, T., Murdoch, R., Bakker, D.C.E., Bowie, A.R., Buesseler, K.O., Chang, H., Charette, M., Croot, P., Downing, K., Frew, R., Gall, M., Hadfield, M., Hall, J., Harvey, M., Jameson, G., LaRoche, J., Liddicoat, M., Ling, R., Maldonado, M.T., McKay, R.M., Nodder, S., Pickmere, S., Pridmore, R., Rintoul, S., Safi, K., Sutton, P., Strzepek, R., Tanneberger, K., Turner, S., Waite, A., Zeldis, J., 2000. A mesoscale phytoplankton bloom in the polar Southern Ocean stimulated by iron fertilization. Nature 407, 695–702.

Boyd, P.W., Crossley, A.C., DiTullio, G.R., Griffiths, F.B., Hutchins, D.A., Queguiner, B., Sedwick, P.N., Trull, T.W., 2001. Control on phytoplankton growth by iron supply and irradiance in the Subantarctic Southern Ocean: experimental results from the SAZ project. Journal of Geophysical Research 106, 31,573–31,584.

Cromwell, T., 1953. Circulation in a meridional plane in the central equatorial Pacific. Journal of Marine Research 12, 196–213.

Dale, B., 1983. Dinoflagellate resting cysts: 'benthic plankton'. In: Fryxell, A.G. (Ed.), Survival, Strategies of the Algae. Cambridge University Press, New York, pp. 69–136.

De Baar, H.J.W., De Jong, J.T.M., Bakker, D.C.E., Löscher, B., Veth, C., Bathmann, U., Smetacek, V., 1995. Importance of iron for plankton blooms and carbon dioxide drawdown in the Southern Ocean. Nature 373, 412–415.

De Pol-Holz, R., Ulloa, O., Dezileau, L., Kaiser, J., Lamy, F., Hebbeln, D., 2006. Melting of the Patagonian Ice Sheet and deglacial perturbations of the N cycle in the eastern South Pacific. Geophysical Research Letters 33. http://dx.doi.org/10.1029/2005GL024477 (L04704).

De Pol-Holz, R., Ulloa, O., Lamy, F., Dezileau, L., Sabatier, P., Hebbeln, D., 2007. Late Quaternary variability of sedimentary N isotopes in the eastern South Pacific Ocean. Paleoceanography 22. http://dx.doi.org/10.1029/2006PA001308 (PA2207).

Esper, O., Zonneveld, K.A.F., 2002. Distribution of organic-walled dinoflagellate cysts in surface sediments of the Southern Ocean (eastern Atlantic sector) between the Subtropical Front and the Weddell Gyre. Marine Micropaleontology 46, 177–208.

Fonseca, T.R., 1989. An overview of the Poleward Undercurrent and upwelling along the Chilean coast. In: Neshyba, S.J., Mooers, C.N.K., Smith, R.L., Barber, R.T. (Eds.), Poleward Flows along Eastern Ocean Boundaries. Springer, New York, pp. 203–228.

François, R., Frank, M., Rutgers van der Loeff, M.M., Bacon, M.P., 2004. ^{230}Th-normalization: an essential tool for interpreting sedimentary fluxes during the late Quaternary. Paleoceanography 19 (PA1018).

Garcia, H.E., Locarnini, R.A., Boyer, T.P., Antonov, J.I., 2010a. World Ocean Atlas 2009 volume 4: nutrients (phosphate, nitrate and silicate). In: Levitus, S. (Ed.), NOAA Atlas NESDIS 71. U.S. Government Printing Office, Washington, D.C., p. 398.

Garcia, H.E., Locarnini, R.A., Boyer, T.P., Antonov, J.I., 2010b. World Ocean Atlas 2009 volume 3: dissolved oxygen, apparent oxygen utilisation, and oxygen saturation. In: Levitus, S. (Ed.), NOAA Atlas NESDIS 70. U.S. Government Printing Office, Washington, D.C., p. 344.

Hebbeln, D., Marchant, M., Freudenthal, T., Wefer, G., 2000. Surface sediment distribution along the Chilean continental slope related to upwelling and productivity. Marine Geology 164, 119–137.

Hebbeln, D., Marchant, M., Wefer, G., 2002. Paleoproductivity in the southern Peru–Chile Current through the last 33 000 yr. Marine Geology 186, 487–504.

Hutchins, D.A., Sedwick, P.N., DiTullio, G.R., Boyd, P.W., Queguiner, B., Griffiths, G.B., Crossley, A.C., 2001. Control of phytoplankton growth by iron and silicic acid availability in the Subantarctic Southern Ocean: experimental results from the SAZ project. Journal of Geophysical Research 106, 31,559–31,572.

Ingle, J.C., Keller, G., Kolpack, R.L., 1980. Benthic foraminiferal biofacies, sediments and water masses of the southern Peru–Chile Trench area, southeastern Pacific Ocean. Micropaleontology 26, 113–150.

Iriarte, J.L., González, H.E., Liu, K.K., Rivas, C., Valenzuela, C., 2007. Spatial and temporal variability of chlorophyll and primary productivity in surface waters of southern Chile (41.5–43°S). Estuarine, Coastal and Shelf Science 74, 471–480.

Kienast, S.S., Calvert, S.E., Pedersen, T.F., 2002. N isotope and productivity variations along the northeast Pacific margin over the last 120 kyr: surface and subsurface paleoceanography. Paleoceanography 17. http://dx.doi.org/10.1029/2001PA000650.

Kienast, M., Lehmann, M., Timmermann, A., Galbraith, E., Bolliet, T., Holbourn, A., Normandeau, C., Laj, C., 2008. A mid-Holocene transition in the nitrogen dynamics of the western equatorial Pacific: evidence of a deepening thermocline? Geophysical Research Letters 35. http://dx.doi.org/10.1029/2008GL035464 (L23610).

Lamy, F., Hebbeln, D., Röhl, U., Wefer, G., 2001. Holocene rainfall variability in southern Chile: a marine record of latitudinal shifts of the Southern Westerlies. Earth and Planetary Science Letters 185, 369–382.

Lamy, F., Kaiser, J., Ninnemann, U., Hebbeln, D., Arz, H., Stoner, J., 2004. Antarctic timing of surface water changes off Chile and Patagonian ice sheet response. Science 304, 1959–1962.

Lamy, F., Kaiser, J., Arz, H.W., Hebbeln, D., Ninnemann, U., Timm, O., Timmermann, A., Toggweiler, J.R., 2007. Modulation of the bipolar seesaw in the Southeast Pacific during Termination 1. Earth and Planetary Science Letters 259, 400–413.

Marret, F., de Vernal, A., Benderra, F., Harland, R., 2001. Late Quaternary sea-surface conditions at DSDP Hole 594 in the southwest Pacific Ocean based on dinoflagellate cyst assemblages. Journal of Quaternary Science 16, 739–751.

Martinez, P., Robinson, R.S., 2010. Increase in water column denitrification during the last deglaciation: the influence of oxygen demand in the eastern equatorial Pacific. Biogeosciences 7, 1–9.

Martinez, P., Lamy, F., Robinson, R.S., Pichevin, L., Billy, I., 2006. Atypical δ15N variations at the southern boundary of the East Pacific oxygen minimum zone over the last 50 ka. Quaternary Science Reviews 25, 3017–3028.

McCulloch, R.D., Bentley, M.J., Purves, R.S., Hulton, R.J., Sugden, D.E., Clapperton, C.M., 2000. Climatic inferences from glacial and palaeoecological evidence at the last glacial termination, southern South America. Journal of Quaternary Science 15, 409–417.

Mitchell, B.G., Brody, E.A., Holm-Hansen, O., McClain, C., Bishop, J., 1991. Light limitation of phytoplankton biomass and macronutrient utilization in the Southern Ocean. Limnology and Oceanography 36, 1662–1677.

Mix, A.C., Tiedemann, R., Blum, P., Shipboard Scientists, 2003. Leg 202 Summary. Ocean Drilling Program, College Station, TX 145.

Mohtadi, M., Hebbeln, D., 2004. Mechanisms and variations of the paleoproductivity off northern Chile (24°S–33°S) during the last 40,000 years. Paleoceanography 19. http://dx.doi.org/10.1029/2004PA001003.

Mohtadi, M., Romero, O.E., Kaiser, J., Hebbeln, D., 2007. Cooling of the southern high latitudes during the Medieval Period and its effect on ENSO. Quaternary Science Reviews 26, 1055–1066.

Mohtadi, M., Rossel, P., Lange, C.B., Pantoja, S., Böning, P., Repeta, D.J., Grunwald, M., Lamy, F., Hebbeln, D., Brumsack, H.-J., 2008. Deglacial pattern of circulation and marine productivity in the upwelling region off central-south Chile. Earth and Planetary Science Letters 272, 221–230.

Morales, C.E., Blanco, J.L., Braun, M., Reyes, H., Silva, N., 1996. Chlorophyll-a distribution and associated oceanographic conditions in the upwelling region off northern Chile during the winter and spring 1993. Deep-Sea Research I 43, 267–289.

Moy, C.M., Seltzer, G.O., Rodbell, D.T., Anderson, D.M., 2002. Variability of El Niño/Southern Oscillation activity at millennial timescales during the Holocene epoch. Nature 420, 162–165.

Naish, T.R., Carter, L., Wolff, E., Pollard, D., Powell, R., 2009. Late Pliocene–Pleistocene Antarctic climate variability at orbital and suborbital scale: ice sheet ocean and atmospheric interactions. In: Florindo, F., Siegert, M. (Eds.), Developments in Earth and Environmental Sciences, 8. Elsevier, Amsterdam, The Netherlands, pp. 465–529.

Ninnemann, U.S., Charles, C.D., 1997. Regional differences in Quaternary subantarctic nutrient cycling: link to intermediate and deep water ventilation. Paleoceanography 12 (4), 560–567.

Pisias, N.G., Heusser, L., Heusser, C., Hostetler, S.W., Mix, A.C., Weber, M., 2006. Radiolaria and pollen records from 0 to 50 ka at ODP Site 1233: continental and marine climate records from the Southeast Pacific. Quaternary Science Reviews 25, 455–473.

Robinson, R.S., Sigman, D.M., DiFiore, P.J., Rohde, M.M., Mashiotta, T.A., Lea, D.W., 2005. Diatom-bound 15N/14N: new support for enhanced nutrient consumption in the ice age subantarctic. Paleoceanography 20. http://dx.doi.org/10.1029/2004PA001114 (PA3003).

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Robinson, R.S., Mix, A., Martinez, P., 2007. Southern Ocean control on the extent of denitrification in the southeast Pacific over the last 70 ka. Quaternary Science Reviews 26, 201–212.

Robinson, R.S., Martinez, P., Pena, L.D., Cacho, I., 2009. N isotopic evidence for deglacial changes in nutrient supply in the eastern equatorial Pacific. Paleoceanography 24. http://dx.doi.org/10.1029/2008PA001702 (PA4213).

Romero, O.E., Kim, J.-H., Hebbeln, D., 2006. Paleoproductivity evolution off central Chile from the Last Glacial Maximum to the Early Holocene. Quaternary Research 65, 519–525.

Saavedra-Pellitero, M., Flores, J.A., Lamy, F., Sierro, F.J., Cortina, A., 2011. Coccolithophores estimates of paleotemperature and paleoproductivity changes in the southeast Pacific over the past 27 kyr. Paleoceanography 26. http://dx.doi.org/10.1029/2009PA001824.

Sarmiento, J.L., Gruber, N., Brzezinski, M.A., Dunne, J.P., 2004. High-latitude controls of thermocline nutrients and low latitude biological productivity. Nature 427, 56–60.

Schneider, W., Fuenzalida, R., Rodríguez-Rubio, E., Garcés-Vargas, J., 2003. Characteristics and formation of Eastern South Pacific Intermediate Water. Geophysical Research Letters 30. http://dx.doi.org/10.1029/2003GL017086.

Shaffer, G., Salinas, S., Pizarro, O., Vega, A., Hormazabal, S., 1995. Currents in the deep ocean off Chile (30°S). Deep-Sea Research 42, 425–436.

Sigman, D.M., Boyle, E.A., 2000. Glacial/interglacial variations in atmospheric carbon dioxide. Nature 407, 859–869.

Sigman, D.M., Altabet, M.A., François, R., McCorkle, D.C., Gaillard, J.F., 1999. The isotopic composition of diatom-bound N in Southern Ocean sediments. Paleoceanography 14, 118–134.

Strub, P.T., Mesias, J.M., Montecino, V., Ruttlant, J., Salinas, S., 1998. Coastal ocean circulation off western South America. In: Robinson, A.R., Brink, K.H. (Eds.), The Global Coastal Ocean: Regional Studies and Syntheses. John Wiley, New York, pp. 273–315.

Thompson, L.G., Davis, M.E., Mosley-Thompson, E., Sowers, T.A., Henderson, K.A., Zagorodnov, V.S., Lin, P.-N., Mikhalenko, V.N., Campen, R.K., Bolzan, J.F., Cole-Dai, J., Francou, B., 1998. A 25,000-year tropical climate history from Bolivian ice cores. Science 282, 1858–1864.

Tsuchiya, M., Talley, L.D., 1996. Water–property distribution along an eastern Pacific hydrographic section at 135°W. Journal of Marine Research 54, 541–564.

Tsuchiya, M., Talley, L.D., 1998. A Pacific hydrographic section at 88°W: water–property distribution. Journal of Geophysical Research 103, 12899–12918.

Verleye, T.J., Louwye, S., 2010a. Late Quaternary environmental changes and latitudinal shifts of the Antarctic Circumpolar Current as recorded by dinoflagellate cysts from off Chile (41°S). Quaternary Science Reviews 29, 1025–1039.

Verleye, T.J., Louwye, S., 2010b. Recent geographical distribution of organic-walled dinoflagellate cysts in the southeast Pacific (25–53°S) and their relation to the prevailing hydrographical conditions. Palaeogeography, Palaeoclimatology, Palaeoecology 298, 219–340.

Verleye, T.J., Pospelova, V., Mertens, K.N., Louwye, S., 2011. The geographical distribution and (palaeo)ecology of *Selenopemphix undulata* sp. nov., a new late Quaternary dinoflagellate cyst from the Pacific Ocean. Marine Micropaleontology 78, 65–83.